

Supporting Information For
**From Pt-rich Dendrites to Ni-rich Cubooctahedrons:
structural evolution and electrocatalytic property studies**

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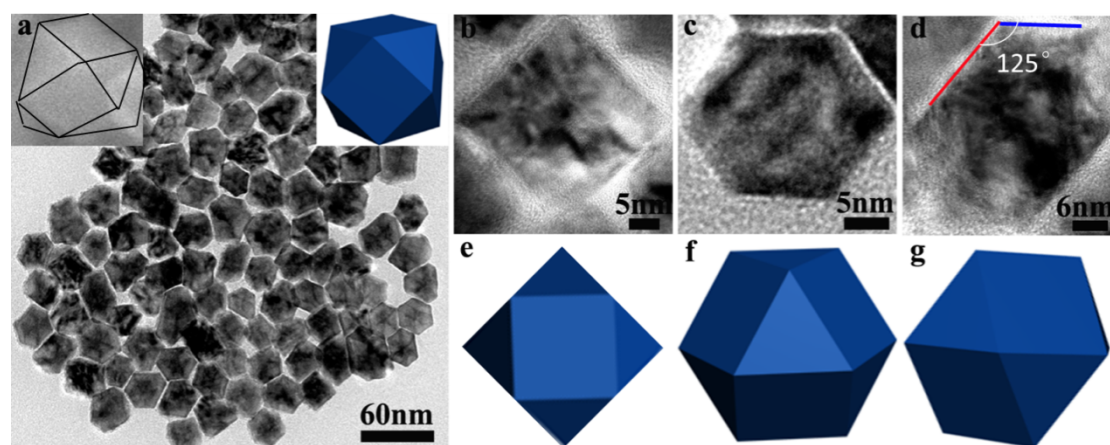


Figure S1 The TEM and 3D modeling schemes illustration of the detailed crystallographic features of the $\text{Pt}_{20}\text{Ni}_{80}$ polyhedrons. (a) survey, (b-d) an individual polyhedron projected from [001], [111] and [110] direction, respectively, (e-g) the corresponding 3D models of the images in (b) to (d), respectively.

	200°C, 5 min	200°C, 30min	200°C, 60 min	200°C, 90 min	220°C, 15min	220°C, 30min	220°C, 60min
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Pt	87.58	78.81	58.79	33.03	40.10	27.38	19.90
Ni	12.42	21.19	41.21	66.97	59.90	72.62	80.10

Table S1 The energy-dispersive X-ray spectroscopy (EDS) data showing the composition of the samples collected at different duration time under different temperature.

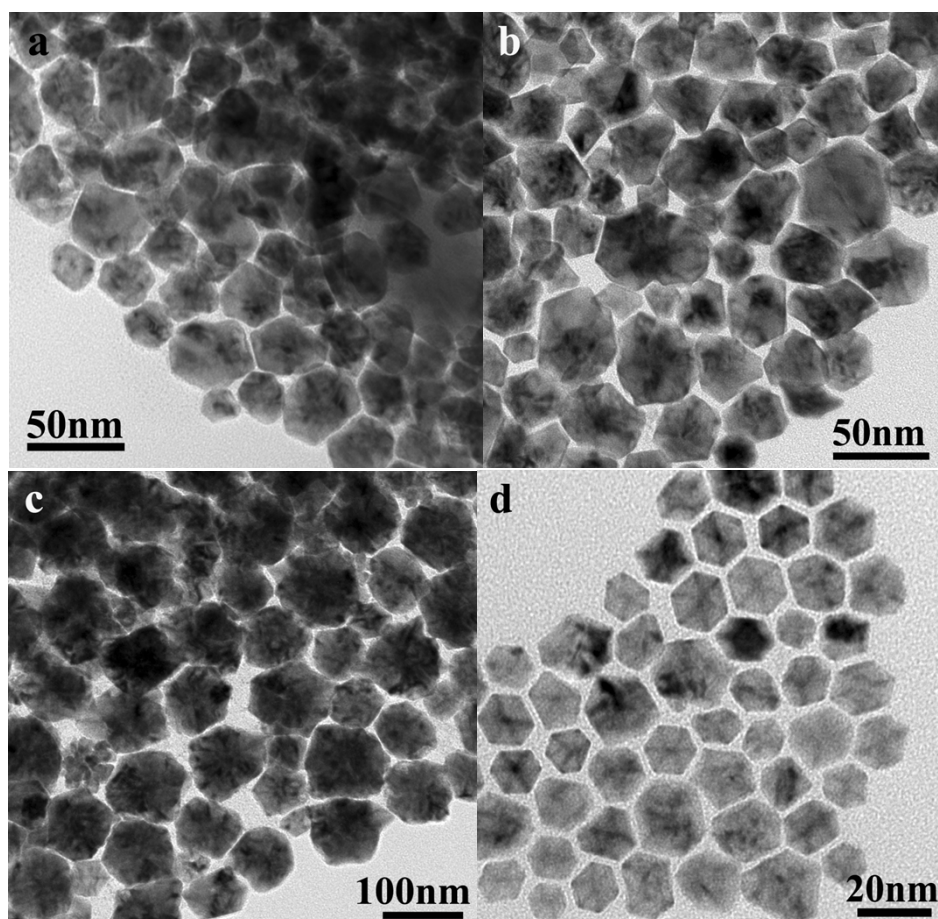


Figure S2 The TEM images of the products obtained in the absence of OA under different temperature and durations. (a) 200 °C, 30 min; (b) 200 °C, 60 min; (c) 200 °C, 90 min; (d) 220 °C, 15 min. It revealed that the as-prepared products exhibited as polyhedrons despite of the time and temperature.

	200°C, 30 min	200°C, 60min	200°C, 60 min	200°C, 90 min	220°C, 15min
Pt	10.8	16.3	22.0	33.03	18.6
Ni	89.2	83.7	78.0	66.97	81.4

Table S2 The energy-dispersive X-ray spectroscopy (EDS) data of the products obtained in the absence of OA under different temperature and durations. (a) 200 °C, 30 min; (b) 200 °C, 60 min; (c) 200 °C, 90 min; (d) 220 °C, 15 min. It revealed that Ni dominated the products and the Pt proportion increase with the reaction proceeding, which is in contrast with these in the presence of OA as discussed in the text.

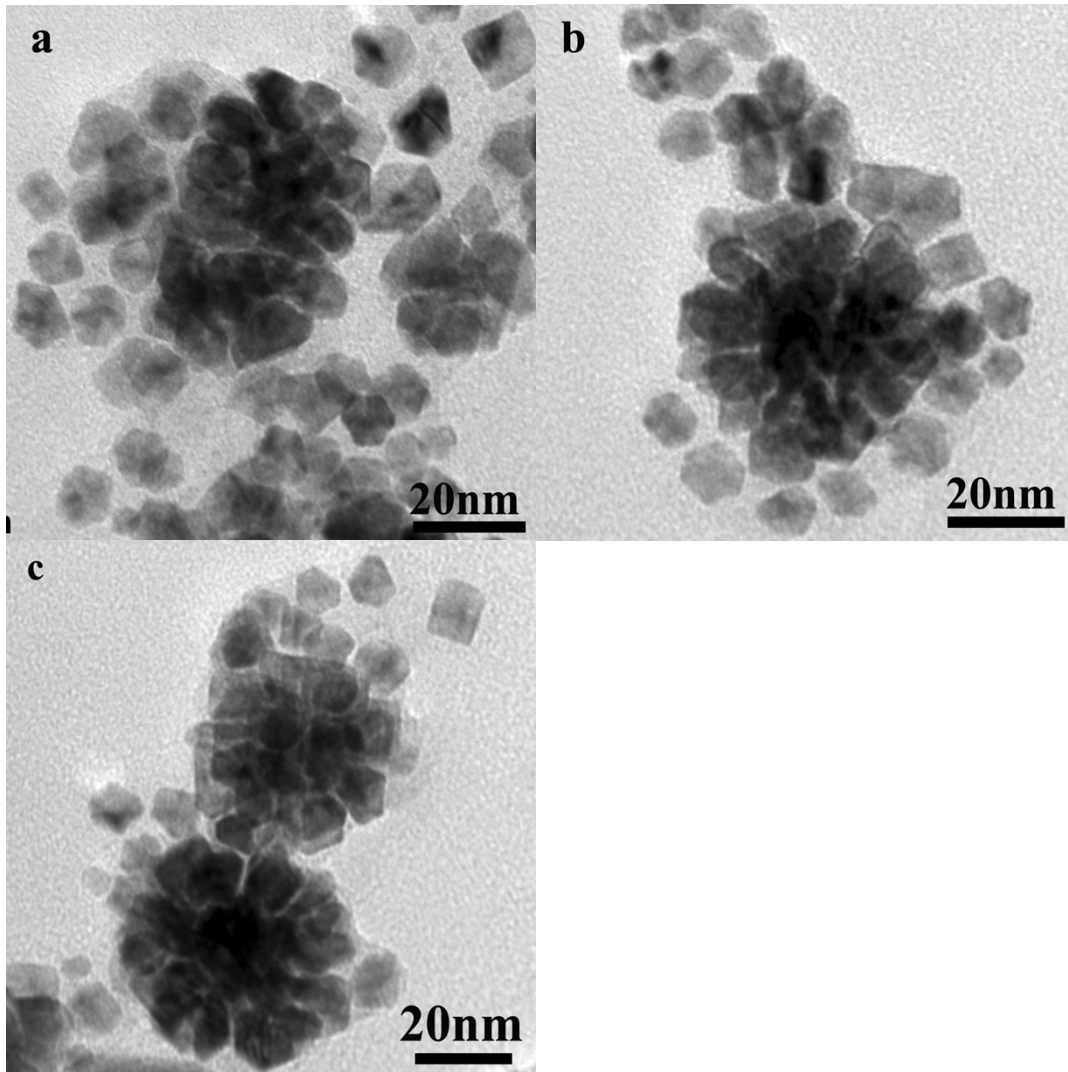


Figure S3 The TEM images recorded at different regions for the products obtained at 200 °C for 80 min, which clearly illustrated the high density of the branch in the dendrites and the identical branch sizes with the isolated particles.

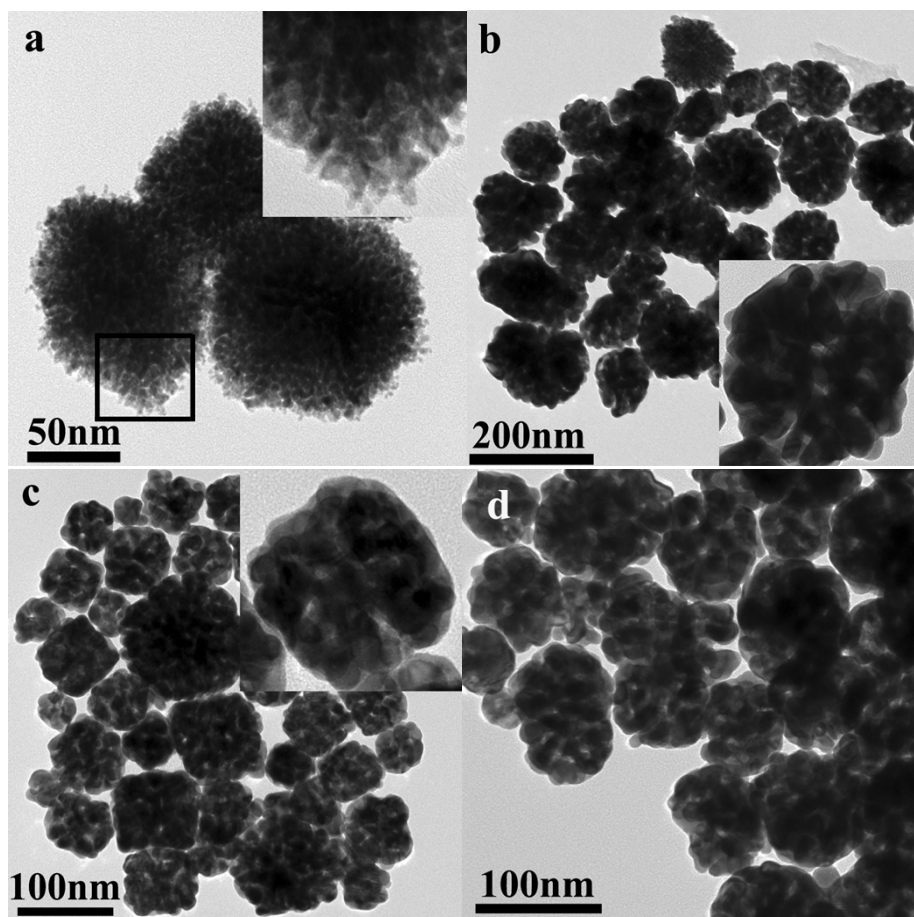


Figure S4 The TEM images of the products obtained in the absence of $\text{Ni}(\text{acac})_2$ while keeping other conditions identical with those for Pt-Ni alloys. (a) 200 °C, 30 min; (b) 200 °C, 60 min; (c) 200 °C, 90 min; (d) 220 °C, 15 min. It revealed that the pure Pt preferred to exhibit as dendritic morphology.

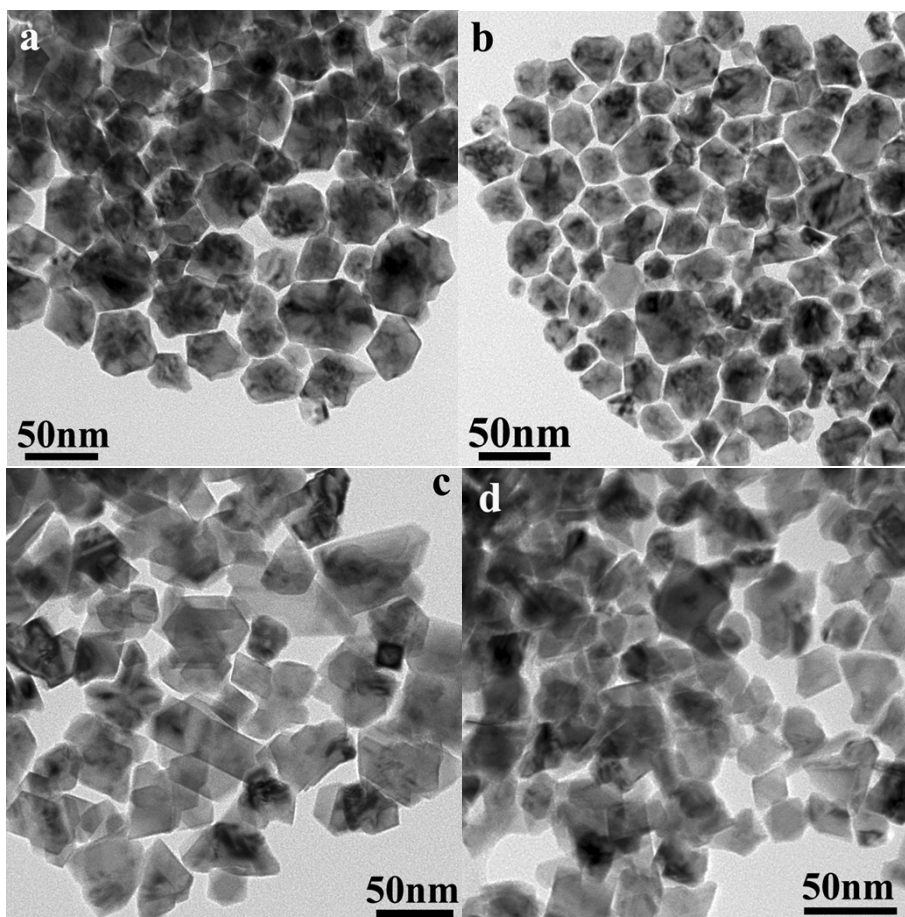


Figure S5 The TEM images of the products obtained in the absence of PtCl_6^{2-} while keeping other conditions identical with those for Pt-Ni alloys. (a) 200 °C, 30 min; (b) 200 °C, 60 min; (c) 200 °C, 90 min; (d) 220 °C, 15 min. It revealed that the pure Ni tended to assume irregular polyhedral shapes.

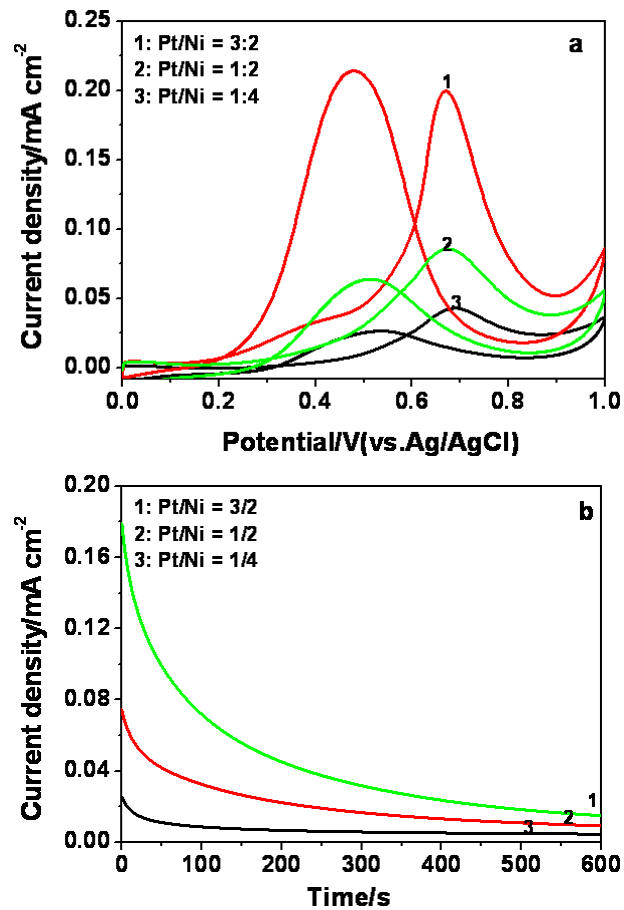


Figure S6 Cyclic voltammograms of Pt/Ni nanoparticle mixture with different ratio in (a) 0.5 mol/L H₂SO₄ + 1.0 mol/L CH₃OH, (b) Chronoamperometry curves of Pt-Ni nanohybrids in 0.5 mol/L H₂SO₄ + 1.0 mol/L CH₃OH at 0.7 V. The scanning rate in all cases is 50 mV/s.